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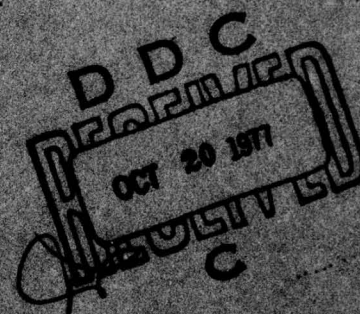
REPORT NO. 2014

## EFFECTS OF HIGH PRESSURE ON MOLECULAR ELECTRONIC SPECTRA: A COMPARISON OF MODELS

Robert C. Tompkins

September 1977

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## I. INTRODUCTION

The influence of pressure on the burning rates of propellants is of great interest to ballisticians. No adequate theoretical model now exists to explain the experimental facts, such as the familiar power law. One approach to this problem is to investigate the pressure dependence of the activation energies of chemical reactions. The rationale is made clear by Figure I, which shows the potential-energy curves (approximated by the harmonic oscillator) along some configuration coordinate,  $Q$ , for the ground (lower curve) and an excited (upper curve) electronic state of a molecule. The activation energy is that which the curves cross on the left. Clearly, pressure effects on the shapes and positions of these curves can change the activation energy. An attempt to derive such a pressure dependence of activation energy from a published model of pressure effects on electronic spectra revealed serious deficiencies in the model. This report covers a study of these deficiencies and a possible remedy.

Drickamer *et al*<sup>1,2</sup> developed a simple and attractive model for the effects of high pressure on molecular, electronic spectra. Okamoto *et al*<sup>3,4,5</sup> proposed and carried out experimental tests of the model. Lin<sup>6</sup> has provided a more rigorous theoretical foundation for the simple model, generalizing it in the process. I shall demonstrate that the experimental tests are inconsistent with the Drickamer model, but not with the Lin theory.

Part II summarizes the Drickamer model and the Okamoto tests. Part III exhibits fallacies in the authors' data analysis and shows that the data, in fact, contradict the model. Part IV summarizes the Lin theory and casts the equations in a form amenable to experimental test. Part V reinterprets Okamoto's data in the context of Lin's theory. The results are discussed in Part VI, and concluding remarks follow in Part VII.

1. Drickamer, H.G., Frank, C.W., and Slichter, C.P., *Proc. Nat. Acad. Sci. (USA)* **69**, 933 (1972).
2. Drickamer, H.G., and Frank, C.W., "Electronic Transitions and the High Pressure Chemistry and Physics of Solids," London: Chapman and Hall (1973).
3. Okamoto, B.Y., Drotning, W.E., and Drickamer, H.G., *Proc. Nat. Acad. Sci. (USA)* **71**, 2671 (1974). Note that  $R$  is misprinted  $R^2$  in the last term of their Eq. (1). The correct equations appears in ref. 4.
4. Okamoto, B.Y., and Drickamer, H.G., *J. Chem. Phys.* **61**, 2870 (1974).
5. Okamoto, B.Y., Thesis, Univ. of Illinois, Urbana-Champaign (1975).
6. Lin, S.H., *J. Chem. Phys.* **59**, 4458 (1973).

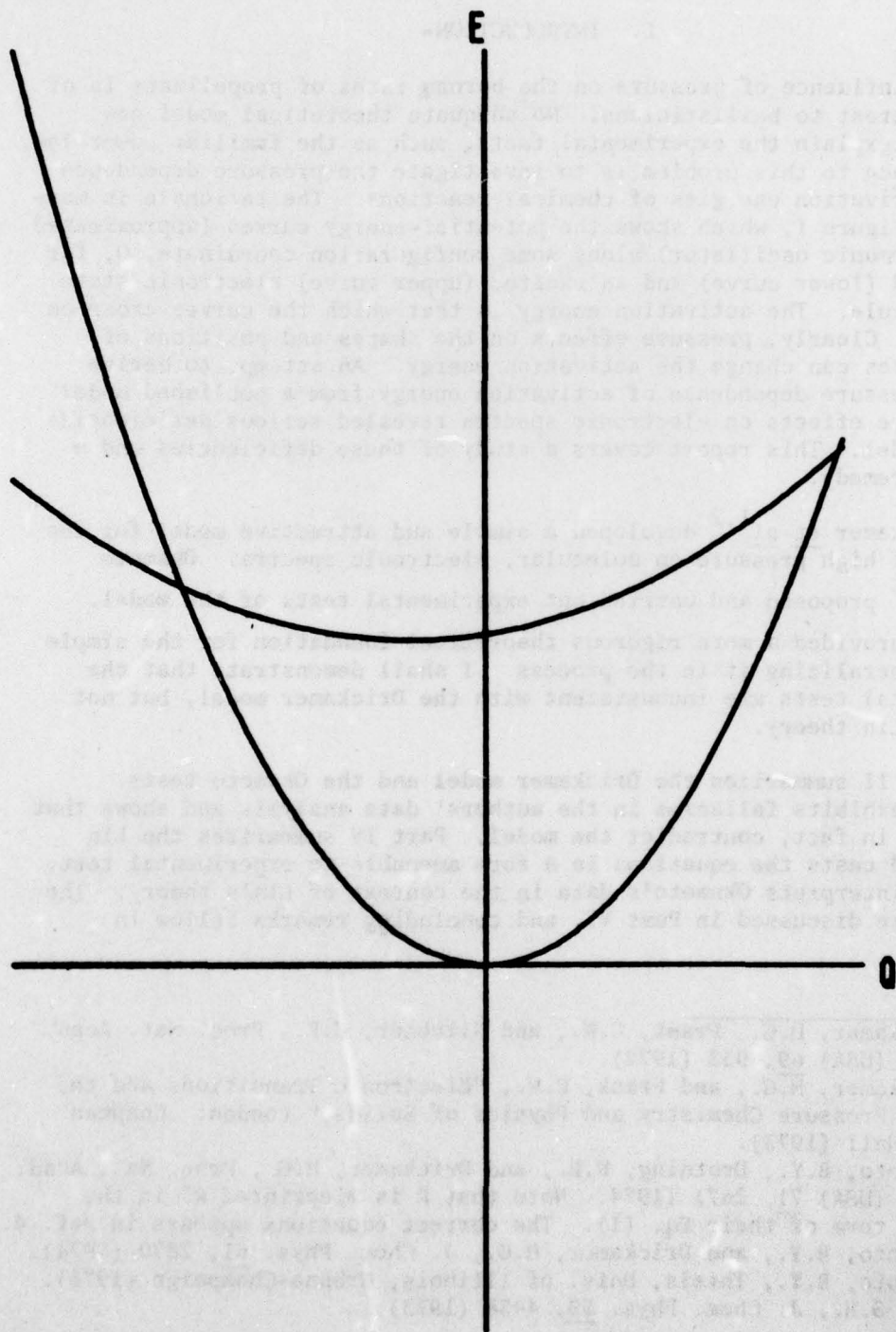


Figure 1. Potential Energy Curves Represented as Harmonic Oscillators.

## II. THE DRICKAMER MODEL

The basic model assumes that pressure couples to harmonic oscillations along a single configuration coordinate, viz., volume. The potential functions for the ground and excited electronic states are then given, respectively, by

$$V = \frac{1}{2}\omega^2 Q^2 + Qp \quad (2.1)$$

and

$$V' = E_0 + \frac{1}{2}\omega'^2 (Q-q)^2 + Qp, \quad (2.2)$$

where  $\omega^2$  is the force constant,  $p$  is pressure,  $Q$  is the configuration coordinate, and  $E_0$  and  $q$  are the energy and coordinate separations, respectively, between the potential minima. Projection of one potential minimum upon the other potential function in accordance with the Franck-Condon principle yields expressions for the optical absorption and emission energies, respectively:

$$\mathcal{E}_a = E_0 + \frac{1}{2}R\omega^2 q^2 + Rqp + \frac{1}{2}(R-1)p^2/\omega^2 \quad (2.3)$$

and

$$\mathcal{E}_e = E_0 - \frac{1}{2}\omega'^2 q^2 + qp/R + \frac{1}{2}(R-1)p^2/(R^2\omega'^2), \quad (2.4)$$

where  $R = \omega'/\omega$ . Similar projection of the terminal points of oscillation of the lowest vibrational level gives the Gaussian half-widths,

$$\epsilon_a = N |R\omega q + (R-1)p/\omega| \quad (2.5)$$

and

$$\epsilon_e = N |\omega q/R^{1/2} + (R-1)p/(R^{3/2}\omega)|, \quad (2.6)$$

where  $N = (8kT \log 2)^{1/2}$ . (References 1 and 2 also generalize the model to multiple configuration coordinates and normal modes, but only the basic form was used by Okamoto.)

Okamoto et al<sup>3</sup> elaborated upon Eqs. (2.3) - (2.6) and proposed a procedure for estimating the unknown parameters from spectral data. They expressed the peak shifts and broadening by

$$\delta\mathcal{E}_a = Rqp + (R-1)p^2/2\omega^2 + \frac{1}{2}Rq^2(\omega^2 - \omega_0^2), \quad (2.7)$$

$$\delta \mathcal{E}_e = qp/R + (R-1)p^2/2R^2\omega^2 - \frac{1}{2}q^2(\omega^2 - \omega_0^2), \quad (2.8)$$

$$\delta \epsilon_a = N(|Rq\omega + (R-1)p/\omega| - |Rq\omega_0|), \quad (2.9)$$

$$\delta \epsilon_e = N(|q\omega/R^{1/2} + (R-1)p/R^{3/2}\omega| - |q\omega_0|), \quad (2.10)$$

where  $\omega^2$  is assumed to be pressure dependent, and  $\omega_0^2$  is the value at atmospheric pressure. The pressure dependence of  $R$  is assumed to be relatively insignificant.

Okamoto and Drickamer<sup>4</sup> experimentally examined the effects of pressures up to 8 GPa on the absorption and emission spectra of anthracene, phenanthrene, and tetracene, both as neat crystals and in various solvents. They found that the data could be fitted by

$$\delta \mathcal{E}_a = a_1 p + a_2 p^2 \quad (2.11)$$

and

$$\delta \epsilon_a = d_a p, \quad (2.12)$$

along with the corresponding expressions with  $e$  substituted for  $a$ .

Okamoto's thesis<sup>5</sup> provides details of the data analysis and lists the experimental parameters. These have been converted to SI units and displayed in Table I. In order to evaluate the parameters of Eqs. (2.7) - (2.10), Okamoto made the further assumption,

$$\omega^2 = \omega_0^2(1 + b_1 p + b_2 p^2), \quad (2.13)$$

where  $b_1$  and  $b_2$  are empirical parameters derived from the compressibility data of Vaidya and Kennedy<sup>7</sup>. Thence he estimated  $R$ ,  $q$ , and  $\omega_0^2$  and concluded that the model was internally consistent.

### III. FALLACIES IN THE OKAMOTO-DRICKAMER RESULTS

Attempts to apply these results in other equations of the model revealed serious discrepancies. Examination of Okamoto's thesis<sup>5</sup> shows that upon substitution of Eq. (2.13) into Eqs. (2.7) - (2.10), certain approximations were made. For example, Eq. (2.7) became

$$\delta \mathcal{E}_a = Rqp + (R-1)p^2/2\omega_0^2 + \frac{1}{2}Rq^2\omega_0^2(b_1 p + b_2 p^2). \quad (3.1)$$

7. Vaidya, S.N., and Kennedy, G.C., J. Chem. Phys. 55, 987 (1971).

TABLE I. Experimental Parameters<sup>a</sup>

	$a_1$ (J/MPa)	$a_2$ (kJ/GPa <sup>2</sup> )	$e_1$ (J/MPa)	$e_a$ (kJ/GPa <sup>2</sup> )	$d_a$ (J/MPa)	$d_e$ (J/MPa)	$a$ (kJ/GPa <sup>2</sup> )	$D_e$ (kJ/GPa <sup>2</sup> )	$E_a$ (J/MPa)	$E_e$ (J/GPa)
Anthracene										
crystal <sup>b</sup>	- 7.07	.23	-13.8	.614	4.76	5.10	1.66	1.90	6.6	6.7
in PMMA	- 3.06	.0822	- 3.62	.145	1.36	1.38	.136	.138	.60	.63
in hexane	- 8.92	3.07	- 9.36	3.39	.821	.728	.0492	.0388	.25	.45
Phenanthrene										
crystal <sup>b</sup>	- 3.09	.122	- 4.5	.0943	2.14	2.52	.335	.465	1.03	1.43
in PMMA	- .91	-.0249	- 1.12	-.177	.531	.65	.0206	.030	.139	.40
in hexane	- 2.70	1.090	- 3.10	.916	.732	.787	.0392	.0452	.160	.26
Tetracene										
crystal	-10.08	.267	-14.2	.900	3.60	c	.947	c	4.7	c

<sup>a</sup>Data of Okamoto<sup>5</sup> converted to SI units.

<sup>b</sup>Polymethyl methacrylate film.

<sup>c</sup>No data available.

In essence he assumed that in the second term on the right hand side,

$$(b_1 + b_2 p)p \ll 1. \quad (3.2)$$

Inasmuch as insertion of the smallest values of  $b_1$  and  $b_2$  used gives a value of 2.3 at only 2 GPa, the assumption is hardly justified. Furthermore, the approximation is unnecessary. The algebra for the full expression is tedious but not difficult.

Another approach, however, is more revealing. It will be convenient first to circumvent the annoying absolute values in Eqs. (2.9) and (2.10). We note that

$$\delta \epsilon^2 \equiv \epsilon^2 - (\epsilon^0)^2 \equiv (\delta \epsilon)^2 + 2 \epsilon^0 \epsilon - (\epsilon^0)^2 \equiv (\delta \epsilon)^2 + 2 \epsilon^0 (\delta \epsilon), \quad (3.3)$$

where  $\epsilon^0$  is the half-width at atmospheric pressure. Eqs. (2.9) and (2.10) are now replaced by

$$\delta \epsilon_a^2 / N^2 = R^2 q^2 (\omega^2 - \omega_0^2) + 2R(R-1)qp + (R-1)^2 p^2 / \omega^2 \quad (3.4)$$

and

$$\delta \epsilon_e^2 / N^2 = q^2 (\omega^2 - \omega_0^2) / R + 2(R-1)qp / R^2 + (R-1)^2 p^2 / R^3 \omega^2. \quad (3.5)$$

For Eq. (2.12) we write

$$\delta \epsilon_a^2 / N^2 = 2E_a p + D_a p^2, \quad (3.6)$$

where  $D_a = d_a^2 / N^2$  and  $E_a = d_a \epsilon_a^0$ , with a similar expression for emission. (This formulation has the additional advantage of utilizing more of the experimental data.) Values for  $D_a$ ,  $E_a$ ,  $D_e$ , and  $E_e$  are given in Table I.

We obtain from Eqs. (2.7), (2.11), (3.4), and (3.6), after simplification,

$$Rq^2 (\omega^2)^2 + 2(Rq - a_1)p - 2a_2 p^2 - Rq^2 \omega_0^2 \omega^2 + (R-1)p^2 = 0 \quad (3.7)$$

and

$$R^2 q^2 (\omega^2)^2 + 2R(R-1)qp - 2E_a p - D_a p^2 - R^2 q^2 \omega_0^2 \omega^2 + (R-1)^2 p^2 = 0 \quad (3.8)$$

These are two quadratic equations in  $\omega^2$  having the same roots for any given value of  $p$ . From the relations between roots and coefficients

$$R(R-1)^2 q^2 p^2 = R^2 (R-1) q^2 p^2, \quad (3.9)$$

whence  $R = 1$ . Making that substitution in Eqs. (3.7) and (3.8), we obtain

$$q^2(\omega^2 - \omega_0^2) + 2(q - a_1)p - 2a_2p^2 = 0 \quad (3.10)$$

and

$$q^2(\omega^2 - \omega_0^2) - 2E_a p - D_a p^2 = 0. \quad (3.11)$$

Having made no assumption as to the functional dependence of  $\omega^2$  upon  $p$ , we have obtained expressions having the form of Eq. (2.13)! Similar analysis for emission yields

$$q^2(\omega^2 - \omega_0^2) + 2(e_1 - p)p + 2e_2p^2 = 0 \quad (3.12)$$

and

$$q^2(\omega^2 - \omega_0^2) - 2E_e p - D_e p^2 = 0. \quad (3.13)$$

We see immediately that

$$D_a = 2a_2, \quad (3.14)$$

$$D_e = -2e_2, \quad (3.15)$$

and

$$a_1 - e_1 = E_a + E_e. \quad (3.16)$$

These relations are not supported by the data in Table I.

We must conclude, therefore, that the experimental data of Okamoto and Drickamer<sup>4</sup> do not support the simple model of Reference 2.

#### IV. THE THEORY OF LIN

Lin<sup>6</sup> considered a solute molecule dissolved in rigid solvent molecules. He wrote a pressure-dependent Hamiltonian for the electronic motion and obtained the potential function for nuclear motion and the electronic wave function by a first-order perturbation. His potential functions for ground and excited states are

$$V = E_0 + \sum_j (\frac{1}{2} \omega_j^2 Q_j^2 + c_j Q_j p) \quad (4.1)$$

and

$$V' = E'_0 + \sum_j \frac{1}{2} \omega_j'^2 (Q_j - q_j)^2 + c_j' Q_j p, \quad (4.2)$$

where  $j$  references the different normal modes and coordinates, and the  $c_j$  are coupling constants. The energy difference between the potential minima (referred to by Drickamer as the thermal energy) is then

$$E_{th}(p) = E_{th}(0) = \sum_j c_j' q_j p + \frac{1}{2} (c_j^2 / \omega_j^2 - c_j'^2 / \omega_j'^2) p^2, \quad (4.3)$$

where  $E_{th}(0) = E'_0 - E_0$ .

These expressions are the same as those given by Drickamer for the general case with one exception, pointed out by Lin. Drickamer implicitly assumed  $c_j' = c_j$ . Lin also noted another difference from Drickamer's treatment, which does not show up in these equations. First-order perturbation theory makes the normal frequencies ( $\omega_j$  etc.) independent of pressure. In what follows I shall follow Lin on these points.

Whereas Drickamer appealed to simple geometric arguments to derive his expressions for the spectral shifts, Lin carried through a full treatment of the band shape function. For the absorption spectra he obtains the following expressions, analogous to Eqs. (2.3) and (2.5),

$$\epsilon_a = E_{th} + \frac{1}{2} \sum_j \omega_j'^2 \delta_j^2 - \frac{1}{2} \hbar \sum_j (\omega_j'^2 / 2 \omega_j^2) (\omega_j - \omega_j') (3 \omega_j - \omega_j') \coth(\hbar \omega_j / 2kT) \quad (4.4)$$

and

$$\epsilon_a^2 = 4 \log 2 \sum_j \omega_j'^2 \left[ \hbar (\omega_j'^2 / \omega_j^2) \delta_j^2 \coth(\hbar \omega_j / 2kT) + (\hbar^2 / \omega_j^2) (\omega_j - \omega_j')^2 \coth^2(\hbar \omega_j / 2kT) \right], \quad (4.5)$$

where

$$\delta_j = q_j + (c_j / \omega_j^2 - c_j' / \omega_j'^2) p \quad (4.6)$$

and  $E_{th}$  is given by Eq. (4.3). The corresponding expressions for emission are obtained by interchanging  $\omega_j$  and  $\omega_j'$  wherever they appear explicitly in Eqs. (4.4) and (4.5) and by changing the signs of the second and third terms on the right-hand side of Eq. (4.4).

Some simplification is necessary before we can make practical use of these equations. Let us, then, make the following two assumptions:

1. The force constants for excited and ground states stand in the same ratio in all normal modes and configuration coordinates, i.e.,  $R_j = \omega_j'^2/\omega_j^2$  can be replaced by  $R$ .

2. The coupling constants for excited and ground states stand in the same ratio in all normal modes and configuration coordinates, i.e.,  $r_j = c_j'/c_j$  can be replaced by  $r$ .

We can now factor  $R$  and  $r$  out of the summations and define the new parameters,

$$\bar{q} = \sum_j c_j q_j \quad (4.7)$$

and

$$1/\bar{\omega}^2 = \sum_j c_j^2/\omega_j^2. \quad (4.8)$$

Remembering that, for small  $x$ ,  $\coth x \approx 1/x$  and making the appropriate substitutions, we obtain

$$\delta \mathcal{E}_a = R\bar{q}p + \frac{1}{2}(R-2r+1)p^2/\bar{\omega}^2 = a_1p + a_2p^2, \quad (4.9)$$

$$\delta \epsilon_a^2/N^2 = 2R(R-r)\bar{q}p + (R-r)^2p^2/\bar{\omega}^2 = 2E_ap + D_ap^2, \quad (4.10)$$

$$\delta \mathcal{E}_e = (Rr+r-R)\bar{q}p/R + \frac{1}{2}r(2R-Rr-r)p^2/R^2\bar{\omega}^2 = e_1p + e_2p^2, \quad (4.11)$$

and

$$\delta \epsilon_e^2/N^2 = 2(R-r)\bar{q}p/R^2 + (R-r)^2p^2/R^3\bar{\omega}^2 = 2E_ep + D_ep^2. \quad (4.12)$$

## V. REINTERPRETATION OF THE OKAMOTO'S DATA IN CONTEXT OF LIN'S THEORY

We have immediately from Eqs. (4.9) - (4.12), for absorption,

$$R\bar{q} = a_1, \quad (5.1a)$$

$$R - 2r + 1 = 2a_2\bar{\omega}^2, \quad (5.2a)$$

$$R(R-r)\bar{q} = E_a, \quad (5.3a)$$

and

$$(R-r)^2 = D_a\bar{\omega}^2; \quad (5.4a)$$

and for emission,

$$(Rr + r - R)\bar{q} = e_1 R, \quad (5.1e)$$

$$r(2R - Rr - r) = e_2 R^2 \bar{\omega}^2, \quad (5.2e)$$

$$(R - r)\bar{q} = E_e R^2, \quad (5.3e)$$

and

$$(R - r)^2 = D_e R^3 \bar{\omega}^2. \quad (5.4e)$$

Of the many possible combinations of these eight equations to estimate the four parameters,  $R$ ,  $r$ ,  $\bar{q}$ , and  $\bar{\omega}$  from the data of Table I, five seemed most straightforward and meaningful.

Method 1 uses only absorption data, Eqs. (5.1a) - (5.4a). Method 2 uses only emission data, Eqs. (5.1e) - (5.4e). Method 3 uses only the shifts in the peaks, Eqs. (5.1a), (5.1e), (5.2a), and (5.2e). Note that either pair of equations, (5.3) or (5.4), yields  $R$  directly. Method 4 uses Eqs. (5.4a) and (5.4e), complemented by (5.1a) and (5.1e). Method 5 uses Eqs. (5.3a) and (5.3e), complemented by (5.1a) and (5.2a). The explicit expressions for the parameters are displayed in the Appendix. Neither Okamoto and Drickamer<sup>4</sup> nor Okamoto<sup>5</sup> reveals the experimental temperature, required to compute  $N$ . However, Mitchell *et al*<sup>8</sup> have recently reported similar experiments in the same laboratory carried out at 297K. I have assumed this temperature in the calculations.

Table II lists the results of the calculations.

## VI. DISCUSSION

The results can be evaluated only in terms of internal consistency. In general the best consistency appears in hexane solution, the poorest in the neat crystals. The most consistent parameter is  $\bar{q}$ , the pressure shift of the configuration coordinate; the least consistent is  $\bar{\omega}$ , the normal frequency. The poor results for  $\bar{\omega}$  can be attributed to small differences between large numbers. The variability in  $R$  and  $r$  suggests that my simplifying assumptions may be too gross.

The experimenters<sup>4</sup> questioned all the emission data for crystalline anthracene and tetracene, and some of those for crystalline phenanthrene because of possible excimer formation. It is surprising, therefore, that Method 1, which uses only absorption data, fails for crystalline

8. Mitchell, D.J., Schuster, G.B., and Drickamer, H.G., J. Am. Chem. Soc. 99, 1145 (1977).

TABLE II. Configuration-Coordinate Parameters

System	R	r	$\bar{q}$ (cm <sup>3</sup> mol <sup>-1</sup> )	$\bar{\omega}$ (10 <sup>7</sup> Pa.J <sup>-1/2</sup> )
<b>Anthracene crystal</b>				
Method 1	-1.09	-.164	6.5	2.3
Method 2	.55	.69	-14.6	.78
Method 3	.65	.89	-10.9	b
Method 4	.96	1.40	- 7.4	1.08
Method 5	.99	1.92	-14.2	b
<b>Phenanthrene crystal</b>				
Method 1	.25	.59	-12.2	1.82
Method 2	.65	.78	- 4.6	1.15
Method 3	.58	.69	- 5.3	3.0
Method 4	.90	1.09	- 3.4	1.10
Method 5	.90	1.23	- 3.6	b
<b>Tetracene crystal<sup>a</sup></b>				
Method 1	- .060	.41	170.3	1.52
Method 2	.76	.89	-13.3	b
<b>Anthracene in PMMA<sup>c</sup></b>				
Method 1	.153	.35	-20.0	1.67
Method 2	.74	.84	- 3.8	1.23
Method 3	.87	.94	- 3.5	b
Method 4	.99	1.08	- 3.1	.78
Method 5	.98	1.17	- 3.3	b
<b>Phenanthrene in PMMA<sup>c</sup></b>				
Method 1	.75	.90	- 1.21	1.67
Method 2	-1.30	-.22	.75	b
Method 3	.83	.92	- 1.10	.90
Method 4	.88	.98	- 1.04	2.1
Method 5	.71	.86	- 1.56	1.57
<b>Anthracene in hexane</b>				
Method 1	.82	.85	-10.8	.40
Method 2	.76	.78	-11.6	.54
Method 3	.94	.96	- 9.5	.133
Method 4	1.08	1.11	- 8.2	.39
Method 5	.83	.85	-13.6	.40
<b>Phenathrene in hexane</b>				
Method 1	.69	.75	- 3.9	.94
Method 2	.76	.80	- 3.6	.92
Method 3	.84	.89	- 3.2	.48
Method 4	.95	1.02	- 2.8	1.08
Method 5	.85	.91	- 4.3	.36

<sup>a</sup>Data not available for Methods 2, 4 and 5.<sup>b</sup>Imaginary value.<sup>c</sup>Polymethyl methacrylate film.

anthracene and tetracene (negative R) and appears to be out of line for crystalline phenanthrene and for anthracene in PMMA. The poor performance of Method 1 is the most puzzling feature of the results.

The theory of Lin<sup>6</sup> promises to provide a useful approach to the study of pressure effects on the electronic structure of complex molecules. It appears already to be a useful qualitative tool, but refinements will be needed to obtain a formulation combining adequate simplicity and accuracy for practical, quantitative applications. Much more experimental data similar to that of Okamoto and Drickamer<sup>4</sup> will be required for a good evaluation.

## VII. CONCLUSIONS

A reexamination of the experimental tests by Okamoto and Drickamer<sup>4,5</sup> of the simple Drickamer model<sup>1,2</sup> of high-pressure effects on electronic spectra revealed errors in the data analysis. Properly interpreted, the tests fail to verify the model. A theory of Lin<sup>6</sup> was found to be more compatible with the data, but it will require further refinement before it is fully adequate for practical applications.

It should now be possible to take a preliminary look at pressure effects on activation energy and perhaps reaction rates, in a qualitative way. Such work is now in progress.

## ACKNOWLEDGEMENT

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## APPENDIX

This Appendix gives the explicit expressions for estimating the configuration-coordinate parameters by the five methods of Part V.

### Method 1

$$(R - r) = E_a a_1 \quad (A.1)$$

$$\bar{\omega}^2 = (R-r)^2 / D_a, \quad (A.2)$$

$$r = 1 - 2a_2 \bar{\omega}^2 + (R-r), \quad (A.3)$$

$$R = (R-r) + r, \quad (A.4)$$

$$\bar{q} = a_1 / R. \quad (A.5)$$

### Method 2

$$(1-\sigma_2)R^3 + R^2 + \sigma_1(2-\sigma_1)R + \sigma_1^2 = 0, \quad (A.6)$$

$$r = R(R+\sigma_1) / [R(R+1) + \sigma_1], \quad (A.7)$$

$$\bar{q} = E_e R^2 / (R-r), \quad (A.8)$$

$$\bar{\omega}^2 = (R-r)^2 / D_e R^3, \quad (A.9)$$

where  $\sigma_1 = e_1 / E_e$ ,  $\sigma_2 = 2e_2 / D_e$ .

### Method 3

$$R^2 = (1-\rho_2) / (\rho_2 - 2\rho_1\rho_2 + \rho_1^2), \quad (A.10)$$

$$r = R(\rho_1 R + 1) / (R + 1), \quad (A.11)$$

$$\bar{q} = a_1 / R, \quad (A.12)$$

$$\bar{\omega}^2 = (R - 2r + 1) / 2a_2, \quad (A.13)$$

where  $\rho_1 = e_1 / a_1$ ,  $\rho_2 = e_2 / a_2$ .

### Method 4

$$R^3 = D_a / D_e, \quad (A.14)$$

$$\bar{q} = a_1 / R, \quad (A.15)$$

$$r = R(e_1 + \bar{q}) / \bar{q}(R+1), \quad (A.16)$$

$$\bar{\omega}^2 = (R-r)^2 / D_a. \quad (A.17)$$

Method 5

$$R^3 = E_a/E_o, \quad (A.18)$$

$$(R-r) = E_a/a_1, \quad (A.19)$$

$$r = R - (R-r), \quad (A.20)$$

$$\bar{q} = E_a/R(R-r), \quad (A.21)$$

$$\bar{\omega}^2 = (R - 2r + 1)/2a_2. \quad (A.22)$$

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